HYDROGEN PRODUCTION FROM THE ACETIC ACID STEAM REFORMING OVER BIMETALLIC NICKEL-COBALT SUPPORTED ON LANTHANUM (III) OXIDE CATALYST

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A dissertation submitted in fulfillment of the requirements for the award of the degree of Master of Engineering (Chemical)

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APRIL 2013

To my beloved parents and brothers

ACKNOWLEDGMENT

I would like to express my sincere gratefulness first of all to Allah for giving me wisdom and strength in my studying. I would like also to take this opportunity to gratefully acknowledge the wholehearted supervision of Dr. Tuan Amran Tuan Abdullah during this work. His dedication, skillful guidance, helpful suggestion and constant encouragement made in possible for me to deliver a dissertation of appreciable quality and standard. I would like thank his kindness, helping me to get through the difficult times and sharing his experience.

Greatest appreciate to my family especially my respectful father, my lovely mother and my kind brothers who gave me full support, patience and understanding, alleviating my family responsibility and encouraging me to concentrate on my study.

Deep thanks to all of the staff of Chemical Engineering department for their support and advices, helping me to reach this far in my project work smoothly.

ABSTRACT

Hydrogen is recognized as a sustainable and renewable energy carrier for transportation. The development of environmental friendly and cost effective hydrogen producing become the main challenge in this area. This work, catalytic steam reforming of acetic acid over bimetallic Nickel-Cobalt (Ni-Co) supported on Lanthanum (III) Oxide (La_2O_3) was studied. The objectives of this study are to obtain a highest hydrogen production and to study the effects of reaction condition such as reaction temperature; pressure and effect the quantity of catalyst to the hydrogen production. Also, to study the effect of Silicon Carbide (SiC) dilution with catalyst at different temperature. The catalysts are prepared by impregnation method. The catalyst performance tests are carried out in a fixed bed reactor at atmospheric pressure and temperature from 500°C to 700°C at increment of 50°C, flow rate range between 0.1 to 0.49 mL/min, acetic acid concentration in range of 10 to 40 wt. % and the weight of catalyst between 0.1 to 0.3 g. It was found that the hydrogen production dropped by increasing of acetic acid concentration and the optimum condition is at temperature of 550 ^{o}C and 0.25 g catalyst whereas 600 ^{o}C while the SiC was used as a catalyst dilution and achieved 98.89% acetic acid conversion. A series of acetic acid flow rate and a series of amount of catalyst supported on La_2O_3 with and without SiC dilution have been investigated at 600 ^{o}C, 1 atm and 10 wt.% of acetic acid. Catalyst at 0.25 gr and 0.36 mL/min of acetic acid flow rate exhibits the best performance; it is given of 0.61 mole fraction of hydrogen.

ABSTRAK

Hydrogen dikenali sebagai sumber tenaga boleh diperbaharui yang mampan kepada pengangkutan. Pembangunan pengeluaran hydorogen yang mesra alam dengan kos yang efektif kini menjadi cabaran penting kepada pengkaji. Kajian ini dijalankan melalui reformasi stim dwilogam diantara acetic mengatasi Nickel-Cobalt (Ni-C0) dan Lanthanum (III) Oxide (La_2O_3). Objektif kajian ini adalah untuk mendapatkan pengeluaran tertinggi hydrogen dan juga bagi mengkaji kesan sampingan dari pencairan Silicon Carbide (SiC) pada tahap suhu yang berbeza. Pemangkin dibuat dengan kaedah impreganasi, manakala kaedah ujian pemangkin dijalankan dalam kaedah wap tetap pada tekanan suhu diantara, 500 ^oC dan 700^oC dan aliran kitaran elektrikal 0.1 – 0.49 mL/minit, konsentrasi asetat diantara 10 sehingga 40 wt% dengan berat pemangkin diantara 0.1 dan 0.3 gram. Hasil kajian mendapati peningkatan hasil hydrogen diperolehi dengan mempertingkatkan konsentrasi asid asetat pada keadaan suhu optimum iaitu 550 ^oC, sementara 600 ^oC SiC diaplikasikan dan berfungsi sebagai pencairan pemangkin. Aliran asis asetat dengan ini disokong pada La_2O_3, atau ketiadaan SiC juga dijakaji pada suhu 600 ^oC, 1 atm dan 10 wt% dari asid asetat. Dapatan kajian juga menunjukkan pemangkin pada 0.25 gram dan 0.36 mL/minit kelajuan aliran asid asetat adalah merupakan pencapaian terbaik seandainya 0.61 fraksi mol hydorogen diberikan.

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LHSV	Liquid hourly space velocity
S/C	Steam to Carbon ratio
HAc	Acetic acid
FPS	Fuel processing system
ATR	Auto thermal reforming
O_2/C	Oxygen to Carbon ratio
HPLC	High performance liquid chromatography
TCD	Thermal conductivity detectors
FID	Flame ionization detectors
RSM	Response Surface Method
SEM	Scanning electron microscopy
TPR	Temperature-programmed reduction
XRD	X-ray diffraction
WGS	Water Gas Shift reaction

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CHAPTER 1

INTRODUTION

1.1 Background of Study

The dependence of world's energy consumption on fossil fuels, especially in the transportation sector leads to a serious energy tension as the increasing energy demand speeds up the drain of the fossil fuel which is finite. Furthermore, combustion of fossil fuel causes the environmental problems. Some problems that have known the most publicity recently are the "greenhouse effect," which is changing the Earth's climate; acid rain that is destroying forests and killing fish; and air pollution that making tens of millions ill and degrading the quality of life in other ways (Mohammed *et al.*, 2011). In order to prevent these dangers, utilization of an alternative source for fossil fuel will be the main focus in this work.

Currently, there is an increasing interest in the use of hydrogen to substitute fossil fuel in the energy business. Hydrogen is a promising energy that potentially plays an important role in future energy systems and replace fossil energy because of its clean burning qualities, its potential for domestic production and the fuel cell vehicles potential for high efficiency. Hence, hydrogen production is a matter of great importance, both in clean fuel production and refinery recently. Therefore for internal combustion engines, hydrogen can be good fuel cells, good possibility fuel and other applications (Yazhong and Hengyong, 2006; Wanga and Cheng, 2012).

Pure hydrogen gas does not exist as a natural resource like oil. It cannot drill for hydrogen or discover it anywhere as a pure gas. Therefore, today hydrogen produced is extracted from natural resources like water, coal gasification, natural gas, acetic acid, glycerol, butanol, ethanol, methane, naphtha catalytic steam reforming and bio-oil. In order to extract hydrogen from these existing resources, energy must be spent. Bio-oil is a preferred hydrogen resource because of its renewable and has environmental benefit characteristics. In the present study, only the main unwanted component of bio-oil which is acetic acid as a source of hydrogen production is chosen (Czernik *et al.*, 2002; Hu and Lu, 2010).

Acetic acid as a source of hydrogen production has been chosen because is one of the major components in bio-oil up to 32 wt.% and a safe hydrogen carrier due to its non-inflammable nature. It is a waste product which is one of the most representative constituents of the water-soluble fraction of bio-oil. Furthermore, the acidity of bio-oil is not suitable for engine fuel because one of the major problems as corrosive resistant materials for engine fuel. In order to solve this problem, the acetic acid in the bio-oil can be separated out and added value in others usage. For example, acetic acid becomes a source in the catalytic steam reforming (SR) for hydrogen production. Hydrogen can be obtained using several technologies such as steam reforming SR, coal gasification, auto-thermal reforming (ATR), dry reforming (DR), partial oxidation (POX), thermolysis and electrolysis (Dahl and Weimer, 2004; Takanabe *et al.*, 2004; Medrano *et al.*, 2008; Neiva *et al.*, 2010).

The proposed method that has chosen for hydrogen production in this study is acetic acid steam reforming. The advantage of this concept is that the steam reforming is the dominant and simple technology for hydrogen production.

Furthermore, steam reforming needs lowest process temperature and higher H_2/CO_2 ratio compare with coal gasification, partial oxidation (POX) and dry reforming (DR). The Nickel/Cobalt supported on Lanthanum (III) Oxide is used inside the reformer to increase the reaction rate because it has been found out that Ni and noble based catalysts were more active and selective towards hydrogen production and gives good hydrogen yields in acetic acid stem reforming. Also, Ni catalysts are promising and not expensive catalysts for bio-oil and biomass gasification. The reactions which may happen during the acetic acid steam reforming are ketonization, methanation, water shift reaction, and thermal decomposition reaction which mentioned in the second chapter of this research (Fatsikostas *et al.*, 2002; Basagiannis and Verykios, 2006; Bulushev and Ross, 2011).

1.2 Problem Statement

Acetic acid constitutes of about 30% of unwanted waste product from bio-oil production. It is an attractive feedstock for hydrogen production as it is non-inflammable in nature and also water-soluble. Thus, hydrogen production from acetic acid steam reforming over bimetallic catalyst has been chosen. However there are some obstacles and difficulties that will be faced during this process. One of these problems is that during steam reforming process, the high temperature (700 to 1000 ^oC) needs to use toward high hydrogen production and high acetic acid conversion. Another problem is the high cost of catalyst due to huge amount usage of catalyst to increase the steam reforming reaction rate. Hence, the selection of low cost catalyst is important for economic process while to ensure the maximum and stability of hydrogen production (Czernik *et al.*, 2002; Takanabe *et al.*, 2004; Medrano *et al.*, 2008).

1.3 Objective of This Work

The objective of the study is to:

i. evaluate the reaction activity of bimetallic nickel (5 wt. %) and Cobalt (5% wt.) supported on Lanthanum (III) oxide on the acetic acid reforming and maximize the hydrogen production at various reaction condition;

ii. study the performance of catalyst on the hydrogen production on the acetic acid steam reforming;

iii. study the effect of reaction catalyst on hydrogen production;

iv. evaluate the effect of silicone Carbide (SiC) as a catalyst dilution on hydrogen production; and

v. compare the experimental analysis result with the thermodynamic analysis results in term of effect of temperature on hydrogen production from the acetic acid steam reforming.

1.4 Scope of Study

The overall scope of this work includes to study the effect of reaction parameter such as temperature (500 ^{o}C to 700 ^{o}C), acetic acid concentration (5 wt.% to 40 wt.%), amount of catalyst (0.1 to 0.3 g), acetic acid flow rate (0.1 to 0.49 mL/min) and stability of catalyst against reaction time (40 to 240 min) on the acetic acid reforming. The reaction conditions used in this work were 1 atm of pressure, 30 mL/min of flow rate of input gas and 600 ^{o}C of temperature.

1.5 Significant of Research

Generally, most of the previous works discussed in detail on the effects of operating parameters on acetic acid reforming reactions using two bimetallic catalysts such as Fe-Co and Ni-Co. Whereas in this study, the catalytic estates of La_2O_3-supported Ni and Co catalysts in acetic acid reforming reactions will be studied. The catalytic behavior between Ni-Co/La_2O_3 and silicone carbide (SiC) as a dilution catalyst were focused. Cobalt and nickel were the widest used transition metals for various steam reforming reactions, and both of them were suggested as appropriate materials because of their maximum catalytic performances. However, the detailed comparisons of Co and Ni catalysts in terms of catalytic behaviors in acetic acid reforming reactions have not yet been recorded. Besides, to our knowledge, the catalytic performances of Ni/La_2O_3 and Co/La_2O_3 catalysts in acetic acid reforming reaction have not been reported in detail. Thus, catalytic behaviors of this La_2O_3-supported transition metals catalyst in steam reforming of acetic acid were aimed in this study.

The study would benefit in a number of particular areas in terms of processing, such as a reduction of energy consumption and expenses of the catalyst, as well as the feed usage. First of all, the study would be able to benefit the minimizing of the energy that used during steam reforming. As mentioned in the problem statement, to increase the hydrogen rate during the steam reforming process, the temperature must be increased, while in this research, the minimum heat (550 ^{o}C) was used during the steam reforming for highest hydrogen yield and highest acetic acid conversion, compare than typical temperature of 700 to 1000 ^{o}C. Also, this research is in significance when using one of the cheapest catalysts which is Nickel and Cobalt supported on Lanthanum (III) Oxide and the less amount of it in terms of highest hydrogen production and acetic acid conversion. Another benefit of this study was to the minimum feed (acetic acid) flow rate was applied toward maximum hydrogen production and acetic acid conversion. The research would be able to provide an idea on diluting the catalyst to increase the hydrogen production as well as acetic acid conversion.

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